

PATENT SPECIFICATION

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(54) A PROCESS FOR MAKING A CALCIUM SILICATE ARTICLE

(71) We, NIPPON ASBESTOS CO., LTD., of 1—26 Shiba Daimon, 1-chome, Minato-ku, Tokyo, Japan, a Japanese Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described, in and by the following statement:—

The present invention relates to a process for making a calcium silicate board or sheet, and in particular to a process for making an asbestos-free calcium silicate board or sheet having excellent properties, comparable to those of calcium silicate board or sheet containing asbestos, by using calcium silicate as a matrix in the absence of asbestos.

Asbestos-containing calcium silicate board or sheet, prepared by paper-making techniques, using asbestos, has been widely used as light non-combustible building material (bulk density=0.7—1.4 g/cm³) since it has a high specific strength, high heat-resistance, fire-resistance and is easily cut with, for example, a saw. Asbestos has contributed to the development of conventional calcium silicate board or sheet to a great extent for the following reasons. Firstly, asbestos fibre has a specific surface area of at least several thousand cm²/g and therefore it sufficiently adsorbs powders of silicic acid (a material containing SiO₂ as its main component) and lime (a material containing CaO and/or Ca(OH)₂ as its main component) which are the starting materials for calcium silicate, and as a result these materials are not lost in the hydration step. Secondly, asbestos has an appropriate filterability (i.e. freeness), and therefore calcium silicate can be easily formed into a board or sheet in combination with asbestos by a paper-making technique. Thirdly, asbestos is highly alkali-resistant, and therefore it does not deteriorate during the production of the board or sheet in the steaming and drying steps, even in the presence of highly alkaline calcium hydroxide. Thus, asbestos plays an important role in the preparation of

calcium silicate board or sheet. Furthermore, since asbestos fibre is not only strong and bulky but also has a high affinity for calcium silicate, the resulting calcium silicate board or sheet has these various advantages.

However, on a worldwide scale, demand for asbestos has rapidly increased and its reserves are being exhausted. Accordingly, the price of asbestos has risen considerably and it has become difficult to obtain the required amounts of asbestos at a reasonable price. In addition to these drawbacks, asbestos has been found to be a carcinogen and therefore its use as an industrial starting material is being limited for health reasons. Furthermore, in the building and ship building industries, a non-combustible building material is required and therefore one (for example, calcium silicate board or sheet) which can be prepared at a relatively low cost and on a large scale is in wide demand. A cheap material that can be prepared by the paper-forming technique is especially desirable. Difficulties have arisen because there is no satisfactory substitute for asbestos in terms of properties and processibility. Therefore, various organic fibres, flax pulp and rayon, and various glassy fibres, for example rock wool, A-glass fibre and E-glass fibre, and mixtures thereof have been considered. Unfortunately these fibres too have disadvantages. Organic fibres have the disadvantage of being combustible, and therefore their use is limited, while glassy fibres have poor alkali-resistance, and therefore cannot be satisfactorily used since they are deformed and their strength is considerably reduced by the presence, in the steaming step, of calcium hydroxide. Recently, an alkali-resistant glassy fibre has been developed and a process for preparing an asbestos-free calcium silicate board or sheet by combining such an alkali-resistant glassy fibre with a small amount of organic fibre has been studied. However, this alkali-resistant glassy fibre has a smooth surface and a poor affinity for other material, and moreover

it is stiff and has poor flexibility. Furthermore, since the consistency of the starting slurry is much thinner in the dehydration-forming process, using the paper-forming technique, than in a press dehydration-forming process, particles of the starting slurry do not remain on the screen but pass through it and are lost. Thus, the filterability of the slurry which is required for the paper-forming technique cannot be attained, and it is therefore very difficult to prepare an asbestos-free calcium silicate board or sheet by means of the sheet-forming technique.

We have now discovered a method of producing a calcium silicate board or sheet, preferably in the absence of asbestos, by the paper-forming technique using calcium silicate as a matrix which overcomes the above disadvantages of conventional processes. This new board has excellent properties, comparable to those of a conventional calcium silicate board or sheet containing asbestos. The specific gravity of the new board or sheet can be adjusted to the desired value.

Thus, the present invention consists in a process for making a calcium silicate board or sheet which comprises forming an aqueous slurry, preferably an asbestos free aqueous slurry, whose solids content comprises silicic acid material, lime material, fibrous wollastonite and pulp, optionally together with a slurry of hydrothermally produced calcium silicate crystals, into a board or sheet steam treating the board or sheet and drying the steam treated board or sheet.

The present invention further consists in a calcium silicate board or sheet when produced by the process of the invention.

The properties of fibrous wollastonite as used in the present invention, are illustrated in Table 1. Fibrous wollastonite imparts an excellent reinforcing effect to the calcium silicate product.

The fibrous wollastonite preferably has a relatively large fibre length, i.e. a median crystal length of at least $19\ \mu$ as determined by granulometry or by sedimentation rate. The amount of the fibrous wollastonite added is preferably from 10 to 40% by weight of the total solid starting material when a slurry of calcium silicate crystal produced hydrothermally is added, and from 10 to 30% when no such calcium silicate crystal is added. If the amount added is less than 10%, a satisfactory processing efficiency and a satisfactory final product cannot be achieved. If the amount of fibrous wollastonite added is greater than 40% in the former case, and 30% in the latter case, it becomes difficult to reduce the specific gravity of the final product, excessive shrinkage by heat occurs and the product becomes brittle and has poor mechanical strength.

TABLE 1.

Chemical formula: CaSiO_3
 Crystal shape: needle-like
 True specific gravity: 2.9
 Expansion coefficient: 6.5×10^{-6} mm/ $^{\circ}\text{C}$
 Melting point: $1,540^{\circ}\text{C}$
 Hue: glossy white
 PH (10% slurry): 9.9.

The pulp used in this invention may be a commercially available pulp for example N-BKP (needle leaf wood bleached kraft pulp), N-UKP (needle leaf wood unbleached kraft pulp), flax pulp or waste paper. The amount of pulp used is preferably from 2% to 10% by weight of the weight of the total solid starting materials since such pulps are combustible. The addition of pulp improves not only dispersibility, adsorption capacity and filterability at the preparation step (of the sheet-forming technique) but also the dry strength of the board or sheet.

Examples of silicic acid material (which, as mentioned above, is a material containing SiO_2 as its main component) used in the process of the invention are siliceous sand, diatomaceous earth, ferrosilicon dust and silicon dust. Ferrosilicon dust is an SiO_2 -containing by-product formed during the production of an iron-silicon alloy, and silicon dust is an SiO_2 -containing by-product formed during the production of Si^0 . These materials typically contain about 89% and 90% by weight of SiO_2 , respectively. The silicic acid material is preferably used in an amount of from 20 to 50% by weight of the total weight of the solid starting materials.

Examples of lime material used in the process of the present invention include slaked lime, quick lime, carbide residue and cement. Carbide residue contains Ca(OH)_2 as its main component and is formed during the production of ethylene from carbide and water. The lime material is preferably used in an amount of 20 to 50% by weight of the total weight of the solid starting materials.

A typical Portland cement contains the following components in the following approximate proportions, expressed as percentages by weight: SiO_2 , 21.7; Fe_2O_3 , 3.2; Al_2O_3 , 5.4; CaO , 64.6; MgO , 1.4; and SO_3 , 1.8.

Calcium silicate crystal slurry produced hydrothermally may be added to obtain a lighter product i.e. one having a specific gravity of 0.7—1.0 — the specific gravity of an asbestos-free calcium silicate board or sheet produced in the absence of hydrothermally produced crystal slurry is generally from 0.7 to 1.4.

The addition of this calcium silicate crystal slurry improves the processability of the product by making it more flexible; the addition

also improves the suitability of the product for sheet-forming by improving the capacity of the fibrous wollastonite to adsorb powdery material. Such crystals of calcium silicate may
5 be prepared by hydrothermally synthesizing silicic acid material and lime material in an autoclave. Their main component is crystals of xonotlite, tobermorite or of both, — see U.S. Patent Specification No. 3,679,446
10 (British Patent Specification No. 1,277,271). Calcium silicate crystal slurry is added in an amount corresponding to a solids content from 1—30%, (preferably from 5—25%) based on the total weight of solid material. If
15 the amount is less than 1%, the desired effects to be produced by the slurry, for example reduction in density, improvement in processability cannot be obtained. If the amount exceeds 30%, filterability is very bad and it
20 is difficult to prepare a board or sheet by means of the sheet-forming technique.

Since the slurry mixture prepared by the process of the present invention comprises
25 fibrous wollastonite, pulp, silicic acid material, lime material and a large amount of water and since particles of the materials adhere to and are adsorbed on the fibrous wollastonite, the slurry can satisfactorily remain on a screen and an appropriate filterability can be obtained. Moreover, dispersibility of these materials is good enough to
30 obtain a satisfactory texture. Thus, the various conditions required in the sheet-forming process are satisfied, and consequently it has become possible to prepare a raw board or
35 sheet of asbestos-free calcium silicate in high yield by means of the usual sheet-forming technique. Such a board or sheet has excellent properties, which are comparable to those of asbestos-containing calcium silicate boards
40 or sheets. The addition of calcium silicate crystal slurry improves the suitability for sheet-forming in the following manner. In the slurry of the mixture of starting materials, particles of silicic acid material and
45 lime material adhere to and are adsorbed onto or are embedded on the calcium silicate crystal gel used as a seed, thereby forming relatively large particles. The particles thus formed are
50 adsorbed in or embedded between fibres of wollastonite and the pulp, and in the dehydration step, the slurry is filtered onto the fibrous wollastonite which acts as a screen. The particles do not block the pores of the fibrous
55 wollastonite but merely increase filtration resistance.

Just prior to the sheet-forming step, an appropriate amount of flocculant for example aluminium sulphate may optionally be added
60 to the slurry in order to accelerate adsorption and agglomeration. Moreover, bentonite or sodium silicate may be added to the slurry in order to control freeness and to improve bonding between layers after rolling.

65 An asbestos-free calcium silicate board or

sheet, prepared by a process according to the present invention has improved heat-resistance, fire-resistance, mechanical strength and processability. A conventional asbestos-containing calcium silicate board or sheet is thin,
70 having a thickness of from 3—15 mm, and as a result it has the disadvantage that cracks are formed on its surface when it is heated, for example in the non-combustibility test (JIS A1321 first grade non-combustibility). If the crack exceeds one tenth
75 of the thickness, it means disqualification for first-grade non-combustibility. However, in the present invention, highly heat-resistant fibrous wollastonite (having a much shorter
80 fibre length than asbestos) or a combination of fibrous wollastonite and highly heat-resistant calcium silicate crystal slurry, is used in the mixture of starting materials. Consequently, the board or sheet is isotropic as
85 regards heat shrinkage, and therefore the size of the cracks is reduced.

Fibrous wollastonite and pulp intimately adhere to the calcium silicate matrix, thereby forming a dense structure due to the reinforcing effect of the fibrous wollastonite and pulp
90 and/or to the binding action by calcium silicate crystal gel. Thus, the asbestos-free calcium silicate board or sheet of the invention is easily prepared by the sheet-forming technique. The board or sheet thus prepared is easily handled and has excellent mechanical strength and processability, for example it is
95 easily cut with a saw, filed or nailed. Crystals of calcium silicate are relatively light, and therefore, the bulk density of the product can be reduced by varying the amount of the calcium silicate added to produce a sufficiently light heat insulation material. In addition to
100 the above advantages, calcium silicate crystals undergo a catalytic reaction under steam treatment (i.e. a hydrothermal reaction) and therefore the saturated water vapour pressure or the steaming time can be reduced. These
105 changes in the hydrothermal reaction conditions can result in a reduction in the production cost, and also prevent organic glassy fibres from being damaged by heat or alkali. This is because the steaming temperature is lowered due to the reduction of the saturated
110 water vapour pressure.

Thus, according to the sheet-forming process, an asbestos-free calcium silicate raw board or sheet, having a good texture, can be produced with high efficiency and high
120 yield using a conventional paper-making machine, and the asbestos-free calcium silicate board or sheet thus produced is light, highly heat-resistant and fire-resistant, and has excellent mechanical strength and processability
125 comparable to a conventional asbestos-containing calcium silicate board or sheet.

The raw board or sheet formed in accordance with the present invention and by the paper-forming technique is subjected to a
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steam treatment in order to complete crystallization of the product of the reaction of the silicic acid and lime material.

5 The steam treatment is preferably conducted under the following conditions:

a) In the case of a board or sheet prepared in the presence of calcium silicate crystal slurry:

10 Saturated Water Vapour
Pressure: 5—18 kg/cm²
Temperature: 151—206°C
Time: 6—20 hrs.

15 b) In the case of a board or sheet prepared in the absence of calcium silicate crystal slurry:

Saturated Water Vapour
Pressure: 7—26 kg/cm²
Temperature: 164—225°C
Time: 7—25 hrs.

20 The present invention is further illustrated by the following Examples.

Examples.

25 Fibrous wollastonite having a median fibre length of 22 μ (such as that manufactured by Interpace Corporation and sold under the trade name of "Wollastonite F-1"), pulp, siliceous sand and slaked lime were mixed together

with and without hydrothermally produced calcium silicate crystal slurry in the weight ratios (on the basis of solid content) shown in Table 2. Water was then added to the above starting materials (10 parts by weight of water to 1 part by weight of solids) and the resultant mixture was fully stirred. During sheet-forming further water was added to the resulting slurry to produce a slurry having a solid concentration of about 3% by weight. The resultant slurry was formed into a raw board by means of the sheet-forming technique. The raw board was then placed in an autoclave and subjected to a steam treatment at 183°C and at a saturated water vapour pressure of 10 kg/cm² for 10 hours. The treated board was then dried.

In a comparative example an asbestos-containing board comprising the ingredients disclosed in Table 2 was prepared by the same method. The calcium silicate crystal slurry used in these Examples was prepared by mixing quick lime and siliceous sand in a CaO/SiO₂ mole ratio of 0.95, adding 15 parts by weight water to 1 part by weight of the mixture to form a slurry and subjecting the slurry to a hydrothermal reaction at 200°C at a saturated water vapour pressure of 15 kg/cm² while stirring for 5 hours.

Various properties of the boards thus produced are shown in Table 2.

TABLE 2

Ingredients (% by weight)	Comparative Example	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
asbestos	22	0	0	0	0	0	0	0
fibrous wollastonite	0	25	25	40	10	20	20	30
pulp	0	6	7	2	6	5	5	2
siliceous sand	13	37	34	29	30	30	33	29
diatomaceous earth	26	0	0	0	0	0	0	0
staked lime	39	37	34	29	29	30	32	29
calcium silicate crystal slurry (solid content)	0	5	0	0	25	15	10	10
Properties suitability for sheet-forming (yield, freeness and texture condition)	good	good	good	good	good	good	good	good
bulk density (g/cm ³)	0.73	0.96	1.12	1.32	0.72	0.80	0.87	0.95
bending strength (normal state kg/cm ²)	166	230	235	250	145	170	195	220
	104	150	155	185	95	110	130	145
residual shrinkage (%) after heating the product at 850°C for 3 hours	1.15	1.23	1.31	1.10	1.22	1.05	1.09	0.01
	3.04	2.54	2.72	2.32	2.35	2.31	2.42	2.02
thickness direction	24.30	5.37	6.43	5.74	3.31	4.46	4.57	4.30
processability (cutting, filing and nailing)	good	good	average	average	good	good	good	good

WHAT WE CLAIM IS:—

1. A process for making a calcium silicate board or sheet which comprises forming an aqueous slurry whose solids content comprises silicic acid material, lime material, fibrous wollastonite and pulp into a board or sheet, steam treating the board or sheet and drying the steam treated board or sheet.
2. A process according to claim 1, in which said aqueous slurry contains no asbestos.
3. A process according to claim 1 or claim 2, in which said aqueous slurry additionally comprises hydrothermally produced calcium silicate crystals.
4. A process according to claim 3, in which said hydrothermally produced calcium silicate slurry constitutes from 1 to 30% by weight of the total solids content.
5. A process according to any of the preceding claims, in which said silicic acid material is siliceous sand, diatomaceous earth, ferrosilicon dust or silicon dust.
6. A process according to any of the preceding claims, in which said lime material is slaked lime, quick lime, carbide residue or cement.
7. A process according to any of the preceding claims, in which said pulp is flax pulp, N-BKP, N-UKP or waste paper pulp.
8. A process according to any of the preceding claims, in which said silicic acid material constitutes from 20 to 50% by weight of the total solids content.
9. A process according to any of the preceding claims, in which said lime material constitutes from 20 to 50% by weight of the total solids content.
10. A process according to any of the preceding claims, in which said pulp constitutes from 2 to 10% by weight of the total solids content.
11. A process according to any of the preceding claims, in which said fibrous wollastonite constitutes from 10 to 40% of the total solids content.
12. A process according to any of the preceding claims, in which said fibrous wollastonite has a median crystal length of at least 19 μ .
13. A process according to any of the preceding claims, which comprises steam treating said board or sheet for from 6 to 25 hours at a temperature of from 151 to 225°C under a saturated water vapour pressure of from 5 to 26 kg/cm².
14. A process according to claim 1, substantially as herein described with reference to any of the foregoing examples.
15. A calcium silicate board or sheet when produced by a process according to any of the preceding claims.

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